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Multiple-distribution DAEM modelling of spruce pyrolysis: an investigation of the best trade-off regarding the number and shape of distributions

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Abstract

The distributed activation energy model (DAEM) is a widely used, accurate and robust method to model biomass pyrolysis. However, the appropriate numerical strategy in terms of distribution number and shape has not been systematically determined. This study analysed spruce powder pyrolysis under different scenarios of multiple-distribution DAEMs with symmetric/asymmetric distributions (Gaussian, logistic and exponential) and different distribution numbers. Dynamic tests at four heating rates (1, 2, 5 and 10 °C/min up to 800 °C) provided solid numerical learning database, and the optimization of residues between numerical calculation and database enabled identification of model parameters. Subsequently, validation was performed with static tests (250 to 500 °C with an interval of 50 °C and 2h-isothermal stages), and their corresponding residue analysis provided a fundamental basis to assess the model's true prediction ability. The trade-off between the model's prediction ability and degrees of freedom was robustly investigated with regard to the number and shape of the distribution. As stated by the quality of validations, a series of Gaussian-DAEMs (distribution number ranged from one to five) allowed for the determination of the best trade-off when the distribution number was three. Finally, the two-Gaussian plus one exponential distribution

29 exhibited the best overall prediction capacity among different multiple-distribution DAEMs,
30 and was confirmed as the best strategy with regard to both distribution shape and number. A
31 DTG simulation investigated each model's simulation effects with three assigned variation
32 sections and justified the correspondence between pseudo-components and biomass
33 constituents. Finally, the DAEM's capability to distinguish the effects of heating rate was
34 demonstrated.

35 Keywords: Pyrolysis, DAEM, Exponential distribution, Gaussian distribution, Trade-off

36

37 **1. Introduction**

38 Biomass pyrolysis receives substantial attention as a key thermal conversion technology
39 in bio-refineries [1] in the production of high value-added chemicals (bio-oil, char and biogas).
40 It also acts as the main initial process for gasification and combustion. The ability to predict
41 constituent kinetics and thermal behaviours during pyrolysis are therefore of great importance,
42 namely for reactor design and industrial scale-up. Thermogravimetric analysis (TGA) is an
43 advanced technology used to study the pyrolysis mechanism relating to devolatilization,
44 which also provides sufficient data for kinetic modelling [2].

45 Pyrolysis is a rather complicated process with numerous chemical reactions, traditional
46 methods of global first- and second-order kinetics are not applicable to biomass pyrolysis [3],
47 which encourages the development of more effective models. Among them, a lumped-kinetic
48 model accounting for more than 30 species has been developed [4], and competitive multi-
49 step models have helped include primary devolatilizations and homogeneous secondary
50 reactions in biomass components [5]. The distributed activation energy model (DAEM) has
51 been proposed to manage the complexity of chemical reactions [6]. In this approach, pyrolysis
52 is assumed to proceed as independently parallel reactions with different activation energies,
53 which are further described by distribution functions.

54 The DAEM has been proposed to be the most comprehensive model to represent the
55 pyrolysis of various complex feedstocks including coal [7], oil shale [8], sewage sludge [9],
56 and biomass [6]. Its prediction kinetics are believed capable of working as sub-models in
57 further industrial simulations [10]. Multiple-distribution DAEM is able to represent major
58 chemical constituents [11] or multiple reaction stages [5], contributing to precise simulations
59 of kinetics. Three-distribution models are widely applied due to its comprehensiveness and
60 excellent correspondence with hemicellulose, cellulose and lignin [12]. Meanwhile the
61 choices of two [13], four [14] and five [15] distributions are also proposed.

62 Concerning the mathematical forms of distribution, continuous statistic distributions are
63 normally applied [15]. Meanwhile finite discrete distribution is also employed, which
64 introduces relations between activation energy and pre-exponential factor either with [16] or
65 without functional forms [17]. Yet differences between these two distribution types could be
66 basically limited, since continuous distributions are necessarily discretized for computational
67 implementations.

68 While symmetric distributions such as Gaussian and logistic have been widely applied in
69 DAEMs [18], asymmetric distributions have also attracted attentions, as partial reactivity
70 distribution in pyrolysis tends to be asymmetric, notably during the final stages [6].
71 Asymmetric distributions, including Weibull and gamma, have been assessed in several
72 studies. Lakshmanan [19] first employed a Weibull DAEM to describe the thermal-chemical
73 kinetics of multiple types of biomass. Recently, Li [20] found the Weibull outperformed other
74 distributions in a study of two- and three-distribution DAEMs in polymer pyrolysis testing of
75 both symmetric and asymmetric distributions. Xu [21] compared single-distribution DAEMs
76 to asymmetric gamma, Rayleigh and Weibull distributions, and found that kinetic parameters
77 relied heavily on distribution form. Alok [22] used asymptotic expansion for gamma
78 distribution's numerical integral in a DAEM, yet the simulation effect was poor. Gamma

79 distribution offers a wide range of shapes that are capable to fit various kinetic profiles. In the
80 decomposition context, its rate parameter measures the average life-time of active component
81 [23], while its shape parameter endows multiple forms. Exponential distribution, as the
82 degeneracy of gamma, shows particular features in lifetime distribution, stochastic process in
83 general [24] and reliability analysis [25]. However, to the best of our knowledge, it has never
84 been employed in multiple-distribution DAEM.

85 The application of multiple-distribution DAEMs has usually focused on the
86 corresponding distribution number with equal pseudo-components or multiple-stage processes
87 [26, 27], yet the effects of distribution number on prediction ability and numerical complexity
88 have received little attention. Indeed, the increase of the distribution number in DAEMs could
89 improve accuracy [15], as more subtle details might be captured in addition to the reaction
90 kinetics. However, the simultaneous growth in numerical complexity could substantially
91 endanger model robustness. Furthermore, the determination of parameters would face local
92 minima or even be meaningless after model identification [28]. On the other hand, single-
93 distribution DAEM shows insufficiency for biomass pyrolysis. In particular, single-Gaussian
94 was found inappropriate to reproduce DTG data [15], and more than one logistic distribution
95 was required for kinetic description [29]. Therefore, regarding the choice of distribution
96 number, a trade-off between a model's prediction capacity and degrees of freedom should be
97 seriously considered.

98 In previous studies, kinetic parameters have generally been determined by single non-
99 isothermal experiments, which introduce the risks of local minima or compensation effects
100 [18]. In this context, multiple experimental data have been proposed to reduce parameter
101 uncertainties, especially those of activation energy and pre-exponential factors [30]. Pyrolysis
102 profiles with two or more heating rates have been proved effective to distinguish between

103 kinetic models [3], and they could mitigate the compensation effect and more closely
104 resemble operations in a genuine industrial system.

105 Generally, identification of model parameters has been based on the principle of
106 minimizing residues between numerical calculations and the learning database, during which
107 advanced optimization algorithms are applied such as the pattern search method [31],
108 differential evolution algorithm [32] and genetic algorithm [33]. Beyond the pursuit of high
109 accuracy and efficiency during model identification, the more important model validations
110 should be emphasized to assess the model's true fit qualities under different reaction
111 conditions. Várhegyi [34] evaluated prediction ability at 40 °C/min with model determined at
112 4 °C/min. Scott [35] extrapolated kinetic parameters that were identified at 20 °C/min and
113 30 °C/min to the theoretical curve at 10000 °C/min. Lin [36] performed predictions for
114 15 °C/min and 25 °C/min with the model that was identified at 20 °C/min. Nonetheless,
115 solid validations with quantifiable uncertainties were relatively rare. Only recently, Ahmad
116 [37] applied artificial neural network (ANN) for validating DAEM accuracy with histogram
117 error distribution. And error analyses, in forms of absolute percentage error (MAPE) and root
118 mean square error (RMSE), were employed in predicting mass loss at different heating rate
119 [38] and biomass type [39] for validation purposes. On the other hand, the kinetic triplets
120 (activation energy, pre-exponential factor and reaction rate) are barely verified since the
121 multiple temperature profiles of parameter determinations couldn't be identical for prediction
122 tests [40]. However, to assess the true model applicability in pyrolysis kinetics, it is logical
123 and necessary to test the fitted parameters against reaction conditions that are different from
124 those used for identification. Therefore, validation with additional temperature profiles should
125 be conducted.

126 This work aims to assess the applicability of the multiple-distribution DAEM
127 considering distribution shape (symmetry/asymmetry), and distribution number using a

128 rigorous approach. To that purpose, a set of dynamic tests were used as learning database and
129 a completely different dataset, consisting of static tests over a wide range of plateau
130 temperatures, was used as a validation database. The best trade-offs between the number of
131 degrees of freedom and the prediction quality will be determined by using up to five-
132 Gaussian distributions. The choice of distribution shape will be tested with two extra DAEMs
133 (three-logistic and two Gaussian + one exponential). Performance of the distributions and its
134 correspondence with biomass constituents will be studied in the subsequent DTG simulations.
135 Finally, DAEM's performance in distinguishing the effect of the heating rate will be analysed.

136

137 **2. Material and methods**

138 **2.1 Material**

139 The biomass used in this study is European spruce (*Picea abies*), a softwood species.
140 A 73-year-old tree was originally cut from the Auvergne region, France and subsequently
141 processed to samples. A tree log 40–50 cm in diameter, 2 m in length was cut 2 m above the
142 bottom. It was cut axially into 2.5-cm thick boards, and a portion 10 cm from the centre was
143 taken to make samples for pyrolysis analysis. A rectangular column 2.5×2.5×5 cm³ was cut
144 from the healthy sapwood part of the board, where wood properties were relatively uniform. It
145 was first sliced and ground in a cutting mill (RETSCH SM300) with a bottom sieve of 1 mm
146 trapezoidal holes, followed by additional grinding with a universal mill (M20-IKA). A sieve
147 stack of 0.063 mm and 0.08 mm opening sizes was used for sieving wood powder in a
148 vibratory sieve shaker (RETSCH AS 200) at an amplitude of 90 % for 30 min. The sieved
149 wood powder between 0.063–0.08 mm was dried at 105 °C for 24 h and stored in a desiccator.

150 Table 1 lists the basic chemical information of spruce sample. The ultimate and
151 proximate analyses of the wood sample (density 450 kg/m³) on a dry basis were conducted
152 using a Thermo Fisher Scientific FLASH 2000 organic elementary analyser and Nabertherm

153 LV/9/11 furnace, respectively, following the ASTM E1755 and E872 standards. The chemical
154 composition analysis was based on the standard method of NREL (National Renewable
155 Energy Laboratory, U.S. Department of Energy).

156 Table 1. Results of proximate, ultimate and chemical composition analyses of European
157 spruce powder on a dry basis

Proximate analysis (wt.%)			Ultimate analysis (wt.%)			Chemical composition (wt.%)		
Volatile	Ash	FC	C	H	O	Cellulose	Hemicellulose	Lignin
84.93	0.29	14.78	47.1	6.0	43.7	42.49	14.89	31.59

158

159

160 2.2 Experimental method

161 Pyrolysis of spruce powder was performed in a thermogravimetric analyser (TGA, STA
162 449 F3 Jupiter, NETZSCH). TG signals were detected at data acquisition intervals of 0.1 min.
163 For each test, a ca. 10-mg sample was evenly spread in an alumina crucible. Measurements
164 were conducted under a pure nitrogen (99.999%) purge and protective gases at 50 ml/min and
165 20 ml/min, respectively.

166 Dynamic tests consisted of four different heating rates (1 °C/min, 2 °C/min, 5 °C/min
167 and 10 °C/min) during the pyrolysis stages. The entire temperature program started by
168 increasing the temperature from 30 °C to 100 °C at 10 °C/min, then maintaining it for 30 min
169 to eliminate the residual water presented in sample. The temperature was linearly increased to
170 800 °C at the four aforementioned heating rates, then cooled to room temperature under the
171 nitrogen purge. The thermogravimetric data from dynamic tests were set as a learning
172 database for the subsequent model identification process.

173 Static tests served as a model validation database. Similar to the dynamic tests above, the
174 wood sample was heated from 30 °C to 100 °C at 10 °C/min and held for 30 min. Then the
175 temperature was raised to the plateau at 10 °C/min, and an isothermal period maintained at

176 this value for 2 h. A series of tests were performed from 250 °C to 500 °C in 50 °C
177 increments (250, 300, 350, 400, 450, 500 °C).

178 Temperature and sensitivity calibrations were performed in advance with standard
179 materials specific to crucible type, temperature rate and gas type. The certified standards
180 (NETZSCH calibration set) include indium, tin, bismuth, zinc, aluminium and silver. A blank
181 was analysed before every test with the same crucible to exclude buoyancy effects and
182 thermal drift. Dimensionless residual mass (DRM) and conversion rate (X_{exp}) were used to
183 manage TG signals as:

$$DRM(t) = \frac{m_t}{m_0} \times 100\%, \quad X_{exp}(t) = 1 - DRM(t) \quad (1)$$

184
185 in which m_t is the remaining mass at time t , and m_0 the dry mass, determined as the mass
186 after the 30-minute plateau at 100 °C.

187 All dynamic and static tests were repeated twice to ensure accuracy. Standard deviations
188 (SD) of all DRM data between two duplicate tests were calculated for verifications, herein
189 table 2 lists two indexes: mean and maximum values of SD. The mean values got very
190 limited range between 0.12% to 0.48%, and the maximum values that represented severe
191 situation, was ranged between 0.30% to 1.81%. They both provided solid proofs of small
192 errors between two duplicates and ensured the repeatability of experimental data.

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198 Table 2. Mean and maximum values of standard deviations (SD) of DRM values in
 199 duplicate tests

Values of SD	Static test						Dynamic test			
	250 °C	300 °C	350 °C	400 °C	450 °C	500 °C	1 °C/min	2 °C/min	5 °C/min	10 °C/min
Mean (%)	0.46	0.13	0.12	0.47	0.48	0.29	0.33	0.26	0.41	0.32
Maximum (%)	0.88	0.30	1.61	1.12	0.73	0.44	1.30	0.98	1.32	1.81

200

201 3. Model formulation

202 3.1 DAEM formulation

203 The distributed activation energy model (DAEM) treats biomass pyrolysis as numerous
 204 parallel and irreversible first-order reactions, among them, decomposition rate of reaction i is:

$$\frac{dV_i(t)}{dt} = k_i(V_i^\infty - V_i(t)) \quad (2)$$

205

206 in which V_i^∞ represents maximum volatile production from reaction i , and $V_i(t)$ is the
 207 generated volatile at time t . Reaction rate constant k_i is defined by the Arrhenius equation
 208 with the pre-exponential factor (A_i) and activation energy (E_i):

$$k_i = A_i \exp\left(-\frac{E_i}{RT(t)}\right) \quad (3)$$

209

210 in which R is a universal gas constant and $T(t)$ is the temperature at time t . The
 211 compensation effects could provide different but equally good-fit sets of parameters, bringing
 212 much inaccuracy in identifications. Therefore, the value of pre-exponential factor is usually
 213 fixed to avoid ill-conditioned parameters, meantime being consistent with the transition-state
 214 theory ($A \approx 10^{11}-10^{16} \text{ s}^{-1}$) [34]. Here, A_i is assumed as constant (A) for all reactions.
 215 $V(t)$ is the total volatile production at time t , and statistical distribution $f(E)$ describes the
 216 activation energy, resulting in the integral form of conversion degree $X(t)$:

$$X(t) = \frac{V(t)}{V^\infty} = 1 - \int_0^\infty \exp\left(-\int_{t_0}^t A e^{-E/RT(t)} dt\right) f(E) dE \quad (4)$$

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Wood is treated as the sum of multiple pseudo-components without any interactions during pyrolysis. Distributions $f_j(E)$ with a different weighting factor $V_{max}(j)$ are assigned to the pseudo-component j in wood ($j \in [1: N_d]$), N_d is the total number of distributions. Superposition of their volatile productions provides the final formulation of biomass conversion degree as:

$$X(t) = 1 - \sum_{j=1}^{N_d} V_{max}(j) \int_0^\infty \exp\left(-A \int_0^t e^{-E/RT(t)} dt\right) f_j(E) dE \quad (5)$$

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3.2 Distribution functions and mathematical implementation

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Two common symmetric distributions, Gaussian and logistic distributions, and one asymmetric distribution, gamma distribution, were used in this study. These distributions in DAEM could represent physically the atomic interactions caused by the variability of macromolecules and their interaction in the cell wall [41]. Table 3 summarizes their mathematical formulas of probability density function (PDF), mean value and standard deviation. Their representative curves are depicted in Figure 1. Gaussian distribution, also known as normal distribution, is formulated by its mean value (E_0) and standard deviation value (σ). Its PDF curve is symmetrical and bell-shaped. Logistic distribution is another important symmetric probability distribution. It resembles Gaussian distribution but has heavier tails (larger kurtosis value) and thinner peaks around the mean value. The gamma distribution is defined by the shape parameter α and the rate parameter β . A minimum activation energy (E_{min}) must be added to obtain sufficient degrees of freedom to define the kinetics. The factor $\frac{E-E_{min}}{E_{min}}$ therefore scales the gamma distribution. The flexibility of the gamma distribution can produce different curve shapes by suitable combinations of its two parameters. For instance, when $\alpha = 1$, the gamma distribution becomes an exponential

239 distribution; when $\alpha = \frac{k}{2}$ (k is nature number) and $\beta = 0.5$, it becomes a Chi-squared
 240 distribution.

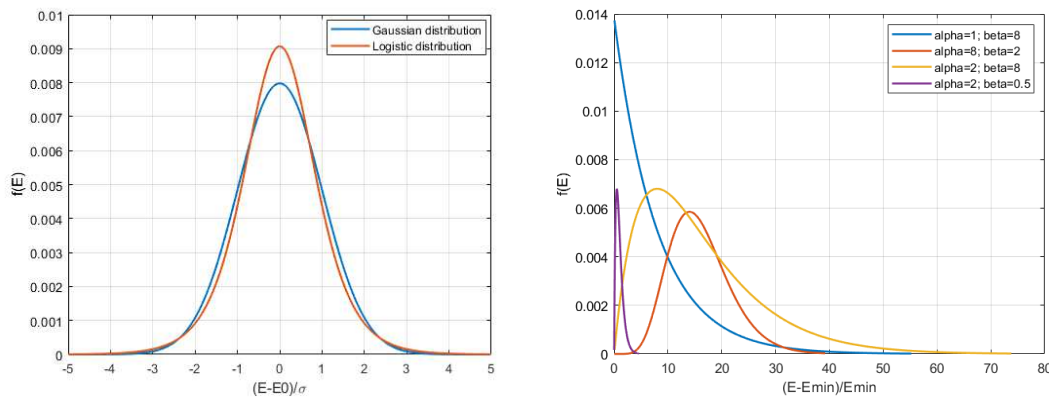
241

242 Table 3. Three types of distribution used in the research

Distributions	PDF	Mean	Standard deviation
Gaussian	$f(E) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(E - E_0)^2}{2\sigma^2}\right]$	E_0	σ
Logistic	$f(E) = \frac{\pi}{\sqrt{3}\sigma} \frac{\exp\left[-\frac{\pi(E - E_0)}{\sqrt{3}\sigma}\right]}{\left\{1 + \exp\left[-\frac{\pi(E - E_0)}{\sqrt{3}\sigma}\right]\right\}^2}$	E_0	σ
Gamma	$f(E) = \frac{\beta^\alpha \left(\frac{E - E_{min}}{E_{min}}\right)^{\alpha-1} \exp\left(-\beta \frac{E - E_{min}}{E_{min}}\right)}{\Gamma(\alpha)}$	$\left(\frac{\alpha}{\beta} + 1\right) E_{min}$	$\frac{\sqrt{\alpha}}{\beta}$

243

244



245

246 Figure 1. Examples of Gaussian, logistic distributions (left) and gamma distributions (right)
 247 with different parameters

248

249 Applying the aforementioned distributions into DAEM, the double integration (over time
 250 and energy) and the lack of an exact analytical solution required multiple precautions.

251 Mathematical implementations were realized using the in-house MATLAB codes, including

252 numerical discretization and integral approximation. The detailed formulation is shown

253 hereafter.

254 **(a) Gaussian distribution**

255 In the discretization of Gaussian distribution, the domain $(-\infty, +\infty)$ changed to finite
256 intervals as $[E_0 - n\sigma, E_0 + n\sigma]$, in which $n = 3$ to ensure 99.9% area coverage (figure 1).
257 Each interval length σ was evenly divided by m to generate fine increments: $dE = \frac{\sigma}{m}$. Prior
258 trials had determined the proper choice of increment number since it might cause solution
259 oscillation with small values and long calculation time with large values [42]. $m = 10$ was
260 found as good compromise for both correct representation of continuous function and
261 concision in algorithm, the discretized activation energy for reaction i became:

$$E_i = E_0 - n\sigma + (i - 0.5)dE, \quad i = [1, 2mn] \quad (6)$$

262

263 The discrete form of Gaussian distribution was therefore presented as:

$$f(E_i) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E_i - E_0)^2}{2\sigma^2}\right) \quad (7)$$

264

265 **(b) Logistic distribution**

266 As in symmetrical distribution, finite intervals $[E_0 - 3\sigma, E_0 + 3\sigma]$ were enough for
267 logistic distribution to ensure 99.9% area coverage. The discretization strategy of activation
268 energy E_i was the same as equation 6, and its discretized function was expressed as

$$f(E_i) = \frac{\pi}{\sqrt{3}\sigma} \frac{\exp\left[-\frac{\pi(E_i - E_0)}{\sqrt{3}\sigma}\right]}{\left\{1 + \exp\left[-\frac{\pi(E_i - E_0)}{\sqrt{3}\sigma}\right]\right\}^2} \quad (8)$$

269 **(c) Gamma distribution**

270 Compared to common symmetric distribution, asymmetric gamma distribution had more
271 complicated numerical implementations. The concepts of minimum (E_{min}) and maximum
272 values (E_{max}) described the discretized activation energy. They formed a finite function

273 domain to avoid extremely large energies which were impossible to appear in decomposition
 274 reactions.

$$E_{max} = E_{min} \cdot \left(1 + \frac{n\alpha}{\beta}\right) \quad (9)$$

275 Here $n = 5$ was set to ensure a distribution function with good representation and
 276 extended in reasonable ranges. Equal partitioning of the whole interval by n_g produced fine
 277 increments dE :

$$dE = \frac{(E_{max} - E_{min})}{n_g} \quad (10)$$

278 in which the fine interval number n_g was set as 100 to ensure accuracy as well as short
 279 solution time. Then gamma distribution discrete normalization form was obtained:

$$f(E_i) = \frac{\beta^\alpha \left(\frac{E_i - E_{min}}{E_{min}}\right)^{\alpha-1} \exp\left(-\beta \frac{E_i - E_{min}}{E_{min}}\right)}{\Gamma(\alpha)} \quad (11)$$

280 The term $\left(\frac{E_i - E_{min}}{E_{min}}\right)^{\alpha-1}$ in gamma distribution demanded preliminary determinations
 281 of discrete strategy, for instance, sudden mutations occurred when α becomes less to the unit,
 282 which produces infinite value at zero ($E_i = E_{min}$), and invalidates the numerical value at the
 283 zero point. Careful prerequisite determinations had been performed which indicated the
 284 optimal choice of the exponential distribution, a degeneracy of gamma, to facilitate model
 285 implementation. The detailed determination process could be found in supporting materials.
 286 Finally, numerical discretization in exponential distribution can be decided as:

$$E_i = E_{min} + (i - 0.5)dE, \quad i = [1, n_g] \quad (12)$$

$$f(E_i) = \beta \exp\left(-\beta \frac{E_i - E_{min}}{E_{min}}\right) \quad (13)$$

287 For every distribution, the characteristic time-constant of the distribution reduced with
 288 the increasing temperature level. For the smallest values of the activation energies, a simple
 289 first-order derivative might fail [43]. To avoid the difficult problem of checking the time-step
 290 for all activation energy values, the effective increment of chemical reaction dV_i was
 291 computed using the exact exponential form [44, 45]:

$$dV = \sum_{j=1}^{N_d} \sum_{i=1}^{N_p} [1 - \exp(-k_i^j dt)] (V_i^{j,\infty} - V_i^j(t)) \quad (14)$$

$$k_i^j = A \exp\left(-\frac{E_i^j}{RT(t)}\right); \quad V_i^{j,\infty} = V_{max}(j) \cdot m_0 \cdot f_j(E_i^j); \quad V_i^j(t=0) = 0 \quad (15)$$

292 in which N_d is the number of distributions, N_p is the number of increment points in each
 293 distribution. E_i^j is the i th activation energy in distribution j . $f_j(E_i^j)$ were determined only
 294 once according to the numerical implementations of every distribution at the initialization
 295 stage of the simulation. During the time-increment, the values of $V_i^j(t)$ were updated and
 296 stored in the calculation loop within the numerical domain. The updated conversion rate $X(t)$
 297 at time t was finally obtained as follows:

$$X(t) = 1 - \frac{\sum_{j=1}^{N_d} \sum_{i=1}^{N_p} \{[1 - \exp(-k_i^j dt)] (V_i^{j,\infty} - V_i^j(t))\}}{m_0} \quad (16)$$

299 Parameter identification was based on the optimization of the objective function, OF ,
 300 which was the residual sum of squares (RSS) between experimental and calculated conversion
 301 rates of all data points alongside the entire reaction history:

$$OF = \sum_{a=1}^{N_{exp}} \sum_{t=0}^{t_f} (X_{exp}(t) - X(t))^2 \quad (17)$$

302

303 in which N_{exp} is the total number of experimental data and t_f is the final reaction time. Here
304 four dynamic tests were analysed simultaneously as a learning database. This wide range of
305 temperature-time pathways together with the large temperature range ensured quasi-complete
306 pyrolysis was likely to provide an accurate and robust parameter determination. Regarding the
307 different number and shape of distributions, their initial parameters were reasonably derived
308 from the relevant literature [6, 26, 41, 46, 47] to avoid local minima in the optimization
309 algorithm. A derivative-free method of the simplex searching algorithm was adopted, and
310 sufficient iterations ensured successful identification by ending with no difference between
311 the penultimate and final optimization values. The whole protocol therefore consists of the
312 following steps: i) choosing a set of reasonable initial parameters, ii) automatic minimization
313 algorithm, iii) perturbation of model parameters to check the robustness of the solution. If a
314 better solution is found at stage iii), steps ii) and iii) are repeated until a stable solution is
315 found.

316 To assess the effect of distribution number, a series of Gaussian-DAEMs was proposed
317 with the distribution number ranging from one to five. Concerning the shape of distributions,
318 three-logistic DAEM and two-Gaussian + one exponential DAEM were further proposed.
319 Herein, only one asymmetric exponential distribution was introduced since it was enough to
320 focus on the performances of high-temperature reactions and provided sufficient flexibility in
321 the model [3].

322 To measure the discrepancy between experimental data and model simulations, two
323 evaluation indexes were applied: root mean square error (RMSE) and the maximum
324 deviations (D_m). They had the same meaning to DRM, aiming to provide comprehensive
325 views on the average and maximum errors in both model identification and validation phases.

$$RMSE = \frac{\sqrt{\sum_{a=1}^{N_{exp}} \sum_{t=0}^{t_f} (X_{exp}(t) - X(t))^2}}{N_{exp}} \quad (18)$$

326

$$D_m = \text{Max}|X_{exp}(t) - X(t)|, \quad \forall t \in [0, t_f] \quad (19)$$

327

328 For the assessment in DTG simulations, dimensionless DTG was defined as the ratio

329 between real-time DTG signal ($\frac{dm}{dt}$) and initial anhydrous mass (m_0):

$$DTG(t) = \frac{1}{m_0} \frac{dm_t}{dt} \quad (20)$$

330 Its local residue ($R_L(t)$) was defined by the differences between calculated ($DTG_{cal}(t)$)

331 and experimental values $DTG_{exp}(t)$:

$$R_L(t) = DTG_{cal}(t) - DTG_{exp}(t) \quad (21)$$

332 With its standard deviation of residue as:

$$\sigma_R = \sqrt{\frac{1}{t_f - 1} \sum_{t=0}^{t_f} (R_L(t) - \bar{R}_L)^2} \quad (22)$$

333

334 4. Results and discussions

335 4.1 Determination of distribution number

336 Figure 2 shows the effects of Gaussian distribution number on both identification and

337 validation stages. Initial sections of DRM curves in identifications were magnified here for

338 comparison among five models; usually, they were challenging to describe numerically

339 because of their very slow kinetics and absence of asymptotic behaviour [48]. In terms of

340 identification stages, one-Gaussian presented very poor overlaps due to its limitations in

341 describing the nature of multiple clusters of reactions [11]. Two-Gaussian demonstrated a

342 slight improvement, yet several noticeable errors still occurred, and the initial stages were

343 poorly produced. For the distribution number from three to five, simulations exhibited quasi-
344 perfect agreements with all experimental data, where most overlaps indicated successful
345 identification. The increase in distribution number represented the increase of pseudo-
346 components, an advanced description strategy of thermal features in multi-step reactions [15].
347 This was further evidenced by the improved simulation accuracy in initial sections, in which
348 error reduction could be observed by increasing distribution number, and almost complete
349 overlap could be realized by five-Gaussian DAEM.

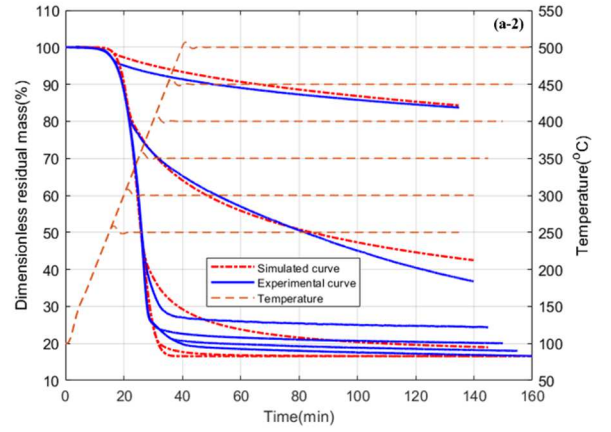
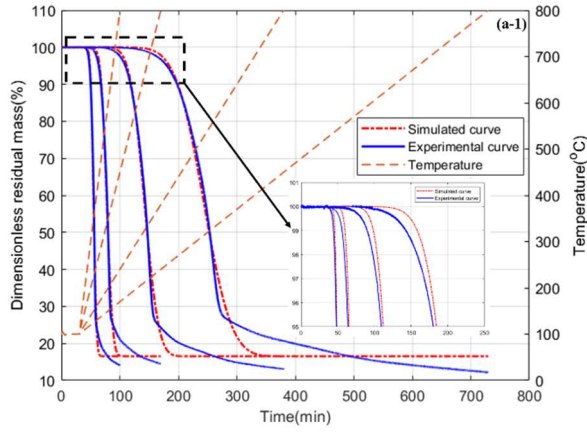
350 For the validation stages, one-Gaussian showed poor predictive ability at all temperature
351 levels, and two-Gaussian also performed unsatisfactorily, with obvious errors from 250 to
352 350 °C. The three-, four- and five-Gaussian showed similarly good predictive abilities,
353 demonstrating excellent overlap during heating periods and only slight deviations in the
354 isothermal plateaus. Major deviations occurred on the curves of 300 °C and 350 °C, while at
355 the other temperatures, the models showed very good predictive abilities throughout the
356 experiments.

357

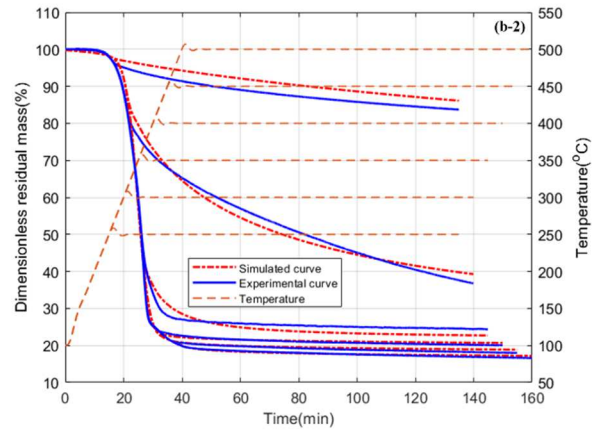
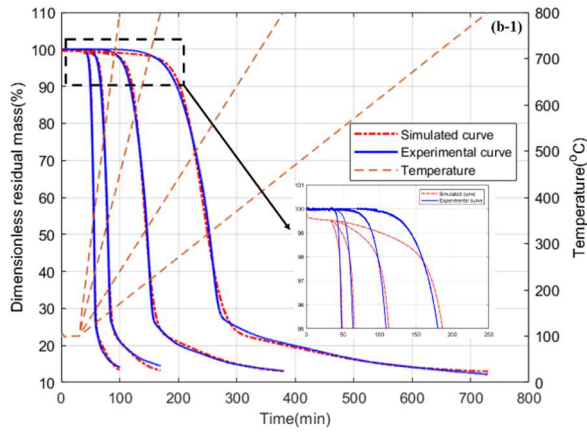
Identification

Validation

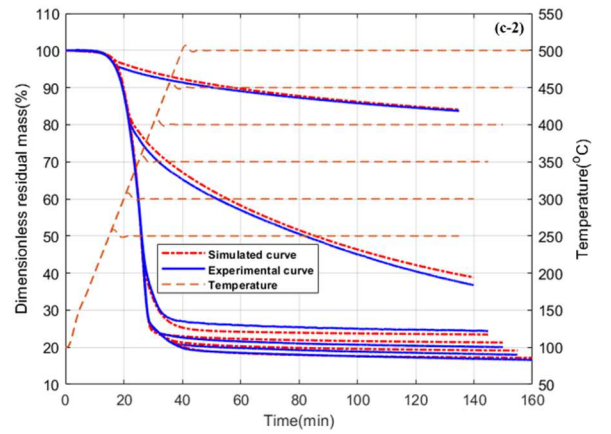
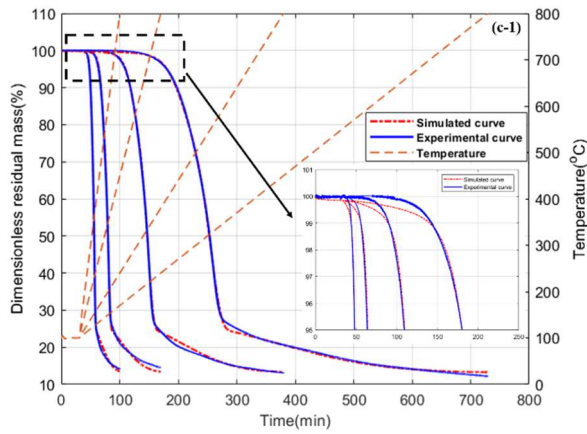
**One-Gaussian
DAEM**



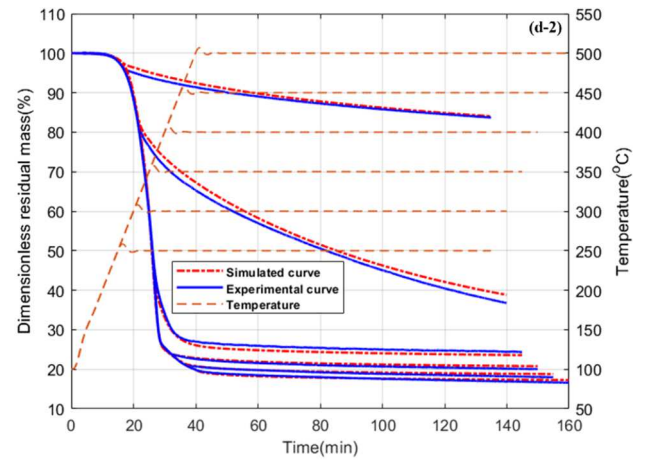
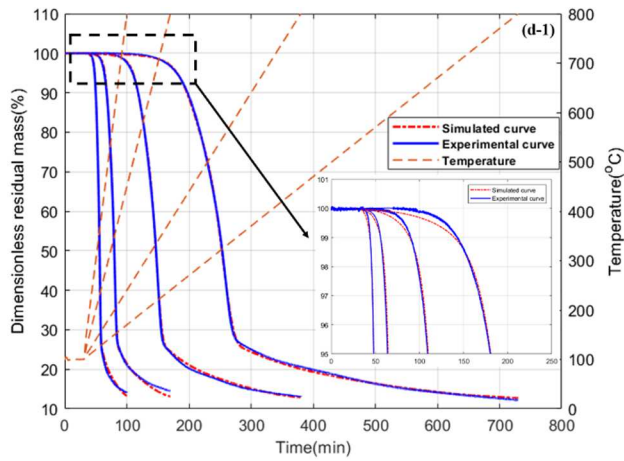
**Two-Gaussian
DAEM**



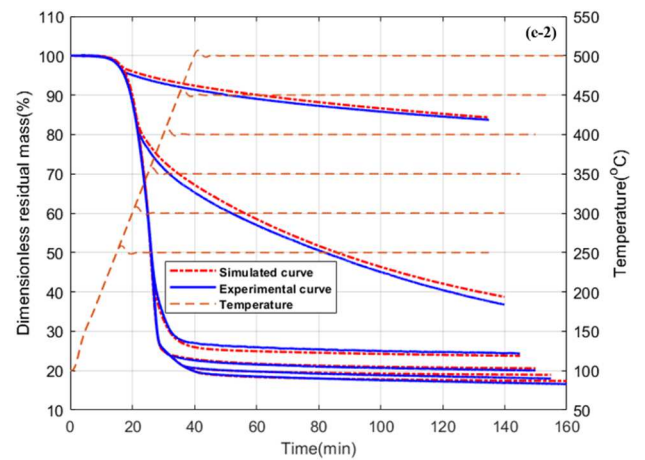
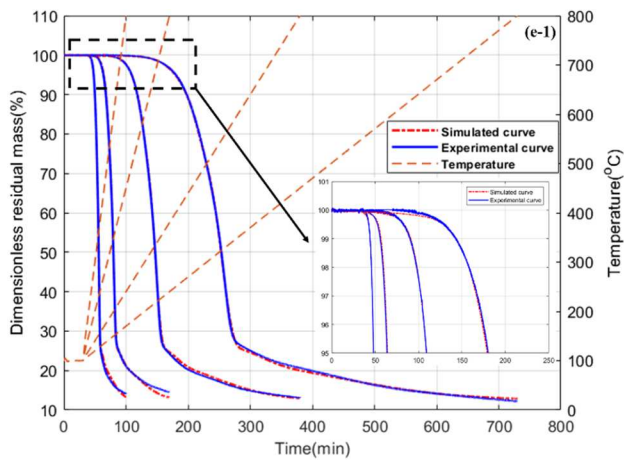
**Three-Gaussian
DAEM**



Four-Gaussian
DAEM



Five-Gaussian
DAEM



358 Figure 2. DRM curves of identification and validation stages and corresponding simulation

359 curves based on identified parameters in multiple Gaussian DAEMs

360 (a) one-Gaussian DAEM, (b) two-Gaussian DAEM, (c) three-Gaussian DAEM, (d) four-
361 Gaussian DAEM and (e) five-Gaussian DAEM

362

363 Identified parameters of five types of Gaussian DAEMs are listed in Table 4. The sum of

364 weighting factors in each model ranged from 0.8345 to 0.8769, which reflected the total

365 content of decomposable species in wood. For one-Gaussian DAEM, its coverage of

366 activation energy was obviously incomplete due to the limitation of distribution number. The

367 two-Gaussian DAEM introduced two distinct distributions that functioned in both low and

368 high activation energy zones. The further increase of distribution number in three-, four- and

369 five-Gaussian DAEM achieved more precise ranges of activation energy. Furthermore,

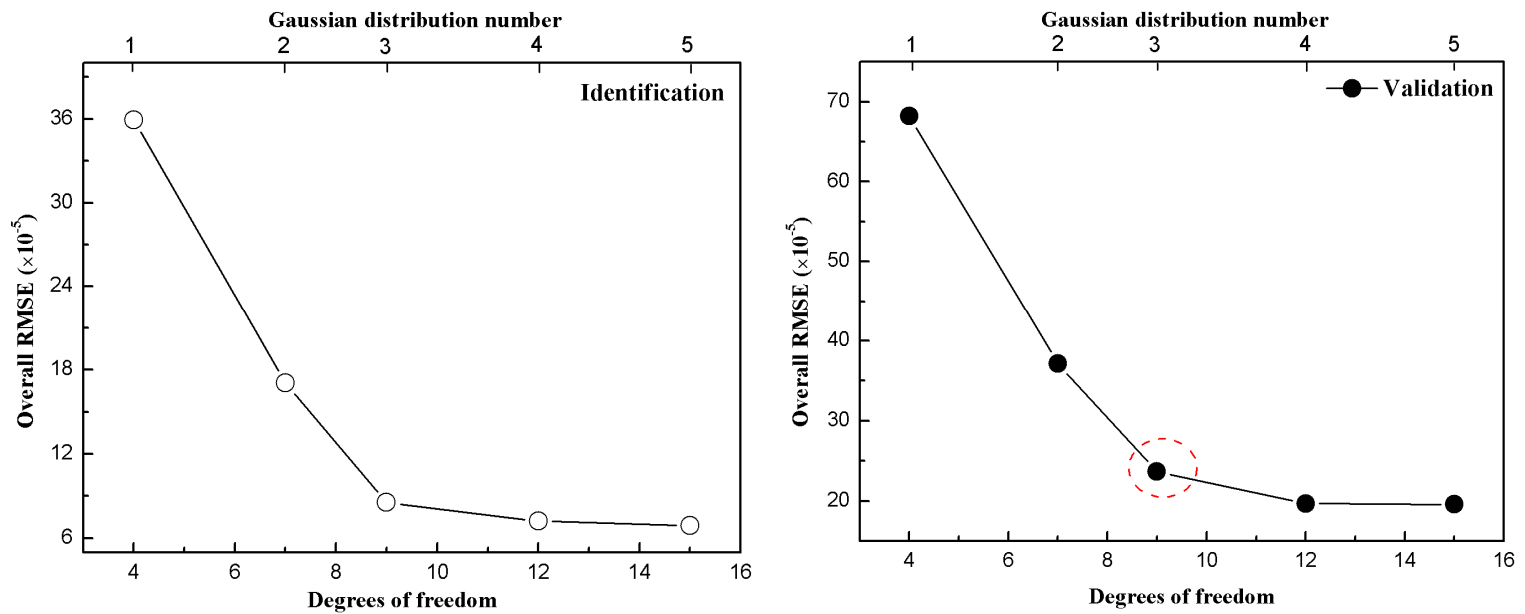
370 complicated repartitions and interactions emerged among multiple distributions. For example,
 371 third and fourth Gaussian distributions were partially overlapped in four-Gaussian DAEM,
 372 and the first and second distributions interacted in five-Gaussian DAEM.

373

374 Table 4. Identified model parameters of five multiple-Gaussian DAEMs

DAEM type	Distributions	V_{max}	$A(\times 10^{13} s^{-1})$	E_0 (kJ/mol)	σ (kJ/mol)
One-Gaussian	1st Gaussian	0.8345	1.56	183.78	10.59
Two-Gaussian	1st Gaussian	0.7153	0.36	175.70	6.74
	2nd Gaussian	0.1574		215.68	54.00
Three-Gaussian	1st Gaussian	0.2125	1.37	170.82	5.77
	2nd Gaussian	0.5001		185.28	1.31×10^{-9}
	3rd Gaussian	0.1553		224.67	45.80
Four-Gaussian	1st Gaussian	0.1660	1.75	170.90	4.21
	2nd Gaussian	0.4954		186.02	6.99×10^{-7}
	3rd Gaussian	0.1205		190.40	25.91
	4th Gaussian	0.0950		259.17	49.18
Five-Gaussian	1st Gaussian	0.0583	1.70	162.40	6.05
	2nd Gaussian	0.1347		172.05	5.74×10^{-3}
	3rd Gaussian	0.5284		185.87	4.01×10^{-4}
	4th Gaussian	0.0347		208.19	6.64
	5th Gaussian	0.1182		244.74	49.57

375



376 Figure 3. Relationships between the model's degrees of freedom and overall RMSE in
 377 identification and validation of multiple-Gaussian-DAEM

378

379 Figure 3 shows the correlations between multiple-Gaussian DAEM's degrees of freedom
 380 (D_f) and overall values of RMSE in both identification and validation stages. Followed by the
 381 increase of the degrees of freedom, the overall RMSE initially decreased rapidly and then was
 382 stable, indicating that prediction ability was effectively improved by increasing the
 383 distribution number to three. Increasing the distribution number to four and five introduced
 384 limited improvements. A high value of D_f inevitably aggravated the numerical complexity,
 385 and a trade-off was, therefore, necessary with respect to the model's prediction ability and
 386 complexity. Using the one-Gaussian DAEM as a reference, the decrease ratios of overall
 387 residue were 45.59%, 65.40%, 71.20% and 71.36%, respectively, for two-, three-, four- and
 388 five-Gaussian DAEMs during the validation stage. Using the three-Gaussian model, the
 389 'inflexion point' (as highlighted with a red circle) was where a significant improvement in
 390 prediction ability was gained with a relatively small increase in D_f . Even though further
 391 increasing distribution number could still promote prediction potential, the disadvantage was

392 that one extra distribution introduced three more kinetic parameters. It was doubtless
393 unnecessary to pursue very limited improvements at the expense of large complexity, or
394 perhaps even worse, a decline in the model's robustness with complicated compensation
395 effects [49]. In this context, the strategy of three Gaussian distributions was the best trade-off
396 between model's complexity and prediction capability.

397 As for the identification process, proposed models showed similar matching
398 relationships between D_f and RMSE, which also demonstrated the good trade-off of the three-
399 Gaussian DAEM. Considering most studies have applied three-distribution DAEMs because
400 they can correlate with main chemical constituents [5, 50], the trade-off strategy herein
401 provides new support for using three distributions in a model.

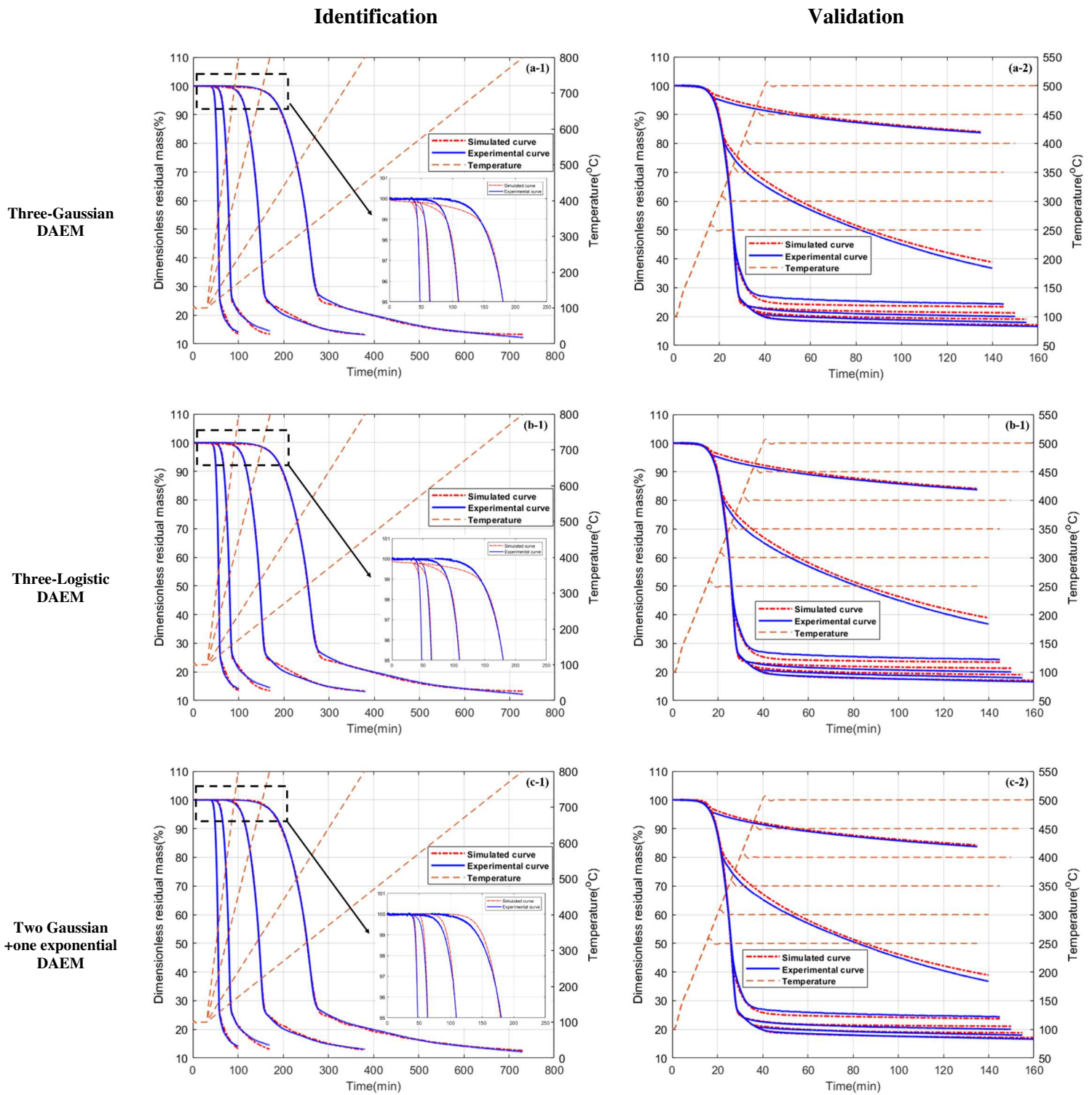
402

403 **4.2 Determination of distribution shapes**

404 **4.2.1 Three-distribution DAEMs**

405 As a three-Gaussian model was determined to be the optimal choice among multiple-
406 Gaussian DAEMs, its counterpart models, three-logistic and two Gaussian + one exponential
407 DAEM, were analysed to determine the shape of the distribution (symmetry/asymmetry).

408 Identification and validation effects of all three-distribution DAEMs are compared in
409 Figure 4. In the general view of identification stages for three models, as expected,
410 simulations exhibited perfect agreements with all experimental data. Three-Gaussian and
411 three-logistic DAEMs had similar negative deviations during the initial stages of simulations,
412 and the two Gaussian + one exponential DAEM modified these plateaus with fewer errors. In
413 the validation stage, the two Gaussian + one exponential DAEM showed noticeable
414 improvements at 400, 450 and 500 °C compared to those of three-Gaussian and three-logistic
415 DAEMs.



416 Figure 4. DRM curves of identification and validation stages and corresponding simulation

417 curves of three types of DAEM

418 (a) three-Gaussian DAEM, (b) three-logistic DAEM and (c) two Gaussian+ one exponential DAEM

419

420 Identified parameters of three models are listed in Table 5. Combinations of distribution
421 shapes made distinctive impacts on model parameters. Compared to the three-Gaussian
422 DAEM, the three-logistic DAEM cut back its second and third weighting factors to
423 compensate on the first. While in the two Gaussian + one exponential DAEM, the second
424 distribution reduced its weighting factor to account for increased first and third distributions.
425 This evident alteration was mainly caused by the third exponential distribution, which spread
426 uniquely in the high activation energy zone due to its asymmetry, and required more
427 weighting factors to more accurately represent chemical reactions at high temperatures.
428 Moreover, all three models maintained their second distribution with the largest weighting
429 factor and narrowest range; this pseudo-component could be correlated to the high content
430 and crystalline nature of cellulose [51].

431 Regarding the nature of chemical collisions in reaction rate equation (eq.3), the
432 activation energy is the barrier of relative translational motion of the reactants [52], and the
433 pre-exponential factor represents the collision frequency that leads to successful reactions. It's
434 therefore only meaningful to analyze the joint effect of these two parameters, which are
435 performed in our model by fixing A as constant, and further distinguish the kinetic variation
436 by different distribution profiles of activation energy. Herein, the excellent fitting quality in
437 multiple experiments, which cover large temperature range and different heating rates, proves
438 that a constant A can effectively represent pyrolysis kinetics over a large range of conditions.
439 Thus, this average meaning of collision frequency among all reactions is meaningful and, in
440 the meantime, keeps the model concise.

441 Cai [6] reviewed three-distribution DAEM in eight types of biomass, where parameter
442 features were quite consistent with corresponding values herein. For instance, $E_{0,1}$ ranged
443 between 169.71 kJ/mol to 186.77 kJ/mol which included our values; the narrowest ranging
444 nature of second pseudo-component and the widest of the third were also confirmed here.

445 Várhegyi [34] tested four biomasses with the three-parallel DEAM, showing similar kinetic
 446 parameters as presented in table 5, especially that $E_{0,2}$ (185 kJ/mol) almost equalled our
 447 identified parameters.

448 Table 5. Identified model parameters of three-distribution DAEM

DAEM type	Distributions	V_{max}	$A(\times 10^{13} s^{-1})$	E_0 or E_{min} (kJ/mol)	σ (kJ/mol)
Three-Gaussian	1st Gaussian	0.2125	1.37	170.82	5.77
	2nd Gaussian	0.5001		185.28	1.31×10^{-9}
	3rd Gaussian	0.1553		224.67	45.80
Three-Logistic	1st Logistic	0.2233	1.43	171.25	6.63
	2nd Logistic	0.4959		185.50	2.51×10^{-6}
	3rd Logistic	0.1496		227.80	48.87
Two Gaussian + one exponential	1st Gaussian	0.2816	1.67	173.19	8.79
	2nd Gaussian	0.4199		186.15	1.66×10^{-7}
	Exponential	0.1940		175.96	$\alpha=1, \beta=0.43$

449

450 4.2.2 Overall model trade-offs

451 Table 6 and 7 list the values of RMSE and D_m among all proposed models during
 452 identification and validation stages, respectively. Herein, the individual and overall values of
 453 RMSE were distinguished by their different data number according to eq. 18. Since the one-
 454 Gaussian and two-Gaussian DAEMs had poor prediction abilities, they will not be discussed
 455 in detail hereafter. The hybrid model type (one Gaussian+ one logistic+ one exponential) was
 456 previously tested, but the numerical complexity and unobvious improvements in simulation
 457 quality didn't encourage us to make further investigations. But still we list its corresponding
 458 data in both table 6 and 7. The main comparisons will be made among the three-distribution
 459 DAEMs (three-Gaussian, three-logistic, and two-Gaussian + one exponential), and four- and
 460 five-Gaussian DAEM.

461 For these models, their identification stages exhibited overall RMSE less than 9×10^{-5} and
 462 the maximum deviations were reasonably small (from 1.02 to 2.74%), acting as solid proof of

463 successful identification. Fit qualities generally increased with a decrease in heating rates and
 464 the smallest D_m always appeared at 1 °C/min, possibly caused by the low fluctuation and
 465 stable temperature profiles at low heating rates, when thermal overshoot was less obvious [53].
 466 The overall identification ability was in the order five-Gaussian > four-Gaussian > two
 467 Gaussian + one exponential > three-Gaussian > three-logistic. Among the three-distribution
 468 DAEMs, asymmetric exponential distribution improved identification accuracy, attributing to
 469 its capability of describing the unique behaviour at high temperatures.

470 Table 6: Parameter identification qualities in the dynamic tests with an average residual
 471 sum of squares and maximum deviations under each heating rate

DAEM type	RMSE ($\times 10^{-5}$)					D_m (%)			
	1°C/min	2°C/min	5°C/min	10°C/min	Overall	1°C/min	2°C/min	5°C/min	10°C/min
One-Gaussian	31.5	35.5	47.2	50.4	35.9	6.50	6.82	6.17	5.26
Two-Gaussian	12.2	17.1	27.9	33.6	17.0	4.16	4.86	4.66	4.29
Three-Gaussian	5.0	8.0	16.6	22.4	8.5	1.68	1.42	1.34	2.71
Four-Gaussian	4.0	6.6	14.4	20.7	7.2	1.21	1.56	1.44	2.59
Five-Gaussian	3.7	6.2	14.2	20.4	6.9	1.02	1.36	1.41	2.49
Three-Logistic	5.2	8.2	16.6	22.5	8.7	1.71	1.46	1.30	2.74
Gaussian + logistic + exponential	4.2	7.1	14.8	21.5	7.6	1.32	1.56	1.43	3.23
Two-Gaussian + one exponential	4.2	7.2	14.8	20.9	7.5	1.27	1.57	1.43	2.54

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Table 7: Validation qualities in the static tests with an average residual sum of squares and maximum deviations under each heating rate

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DAEM type	RMSE ($\times 10^{-4}$)							D_m (%)					
	250°C	300°C	350°C	400°C	450°C	500°C	Overall	250°C	300°C	350°C	400°C	450°C	500°C
One-Gaussian	3.9	6.5	9.7	9.9	6.5	4.3	6.8	2.22	5.71	5.45	5.06	5.09	5.14
Two-Gaussian	7.1	4.7	4.3	2.3	2.3	2.1	3.7	3.12	4.20	3.91	4.00	4.09	4.03
Three-Gaussian	1.8	3.9	3.4	2.3	1.9	1.0	2.4	1.29	2.20	1.99	1.46	1.54	1.51
Four-Gaussian	2.0	3.8	2.5	1.4	1.3	1.1	2.0	1.32	2.24	1.77	1.59	1.53	1.54
Five-Gaussian	2.3	3.9	2.2	1.1	1.4	1.1	2.0	1.12	2.05	1.76	1.50	1.47	1.44
Three-Logistic	1.8	3.9	3.4	2.3	1.9	1.0	2.3	1.22	2.17	2.01	1.42	1.51	1.48
Gaussian + logistic + exponential	1.6	4.1	2.4	1.7	1.3	1.1	2.0	1.22	2.34	1.84	1.73	1.68	1.69
Two-Gaussian + one exponential	1.5	3.8	2.4	1.7	1.3	1.0	1.9	1.22	2.36	1.67	1.60	1.70	1.67

486

487

In the validation of static tests, the models' true prediction potentials were therefore

488

comparable and quantifiable at different temperature levels. The overall RMSE of five

489

compared models ranged between 1.9×10^{-4} to 2.4×10^{-4} , which were plausibly low

490

considering that model parameters originated from dynamic tests without any further

491

identification. Maximum deviations were satisfactorily small in every validation stage of all

492

models. The smallest value appeared at 250 °C (1.12% for five-Gaussian DAEM), and the

493

largest value was at 300°C (2.36% for two Gaussian+ one exponential DAEM); such low

494

values were considered good signs of prediction precision [12, 34]. The accuracy benefits

495

from the comprehensive identification database and numerical training: these two indexes

496

reflected excellent prediction potential for the five DAEM models.

497

Generally, the largest errors occurred at 300 °C and 350 °C among all validation phases,

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yet good fits were found at the other temperature levels. Because parameters were identified

499

over the full pyrolysis condition up to 800 °C, they faced some difficulties in describing

500

incomplete pyrolysis, even though the prediction remained rather good, and was in agreement

501

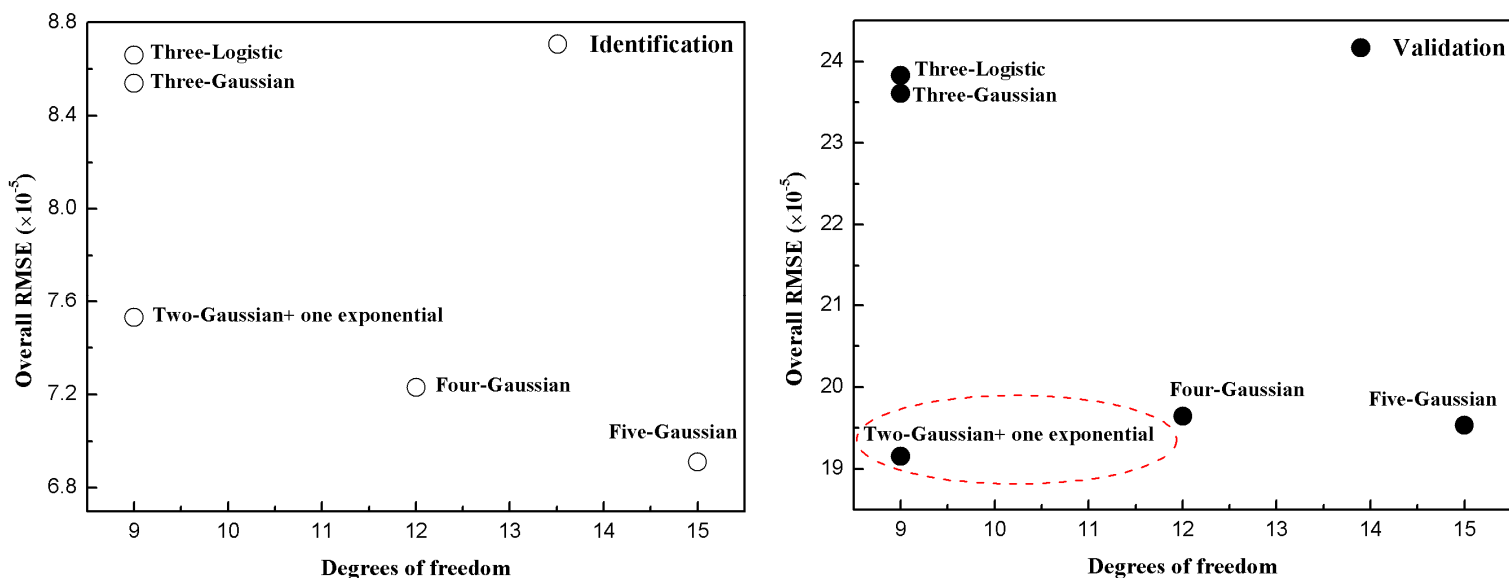
with the literature [54] in which higher simulation errors tended to appear at low temperatures.

502 The mass loss under mild pyrolysis at 250 °C was slow and, in addition, quite well predicted
503 by the DAEM model. These two reasons explain the relatively small errors found for this test.

504 Among these models, overall prediction ability proceeded in the order of two Gaussian
505 + one exponential > five-Gaussian > four-Gaussian > three-Gaussian > three-logistic. Notably,
506 the asymmetric exponential distribution exhibited excellent potential in predicting pyrolysis
507 kinetics with plausible complexity: it provided the lowest RMSE values at 250, 300 and
508 500 °C, and most importantly, the lowest overall RMSE. Due to its asymmetry, exponential
509 distribution expanded uniquely on the side of high activation energy, which only focused its
510 accuracies in high-temperature reactions. In contrast, Gaussian and logistic distributions
511 expanded symmetrically. When they intended to describe large ranges of high activation
512 energies, the symmetry forced distribution to cover the same portion of low values. It
513 conflicted with the distribution that originally represented low activation energy; thus, overall
514 prediction potential was not effectively elevated even with additional symmetric distributions.
515 Beyond that, the increase in distribution number ameliorated identification accuracy in the
516 cases of four- and five-Gaussian DAEMs, yet their overall prediction potentials were not
517 necessarily the best. It was, therefore, indispensable to conduct model identification and
518 validation separately, to obtain correct and comprehensive assessments of the model.

519 The two Gaussian + one exponential DAEM demonstrated its best performances in
520 validation stages, proving a superior strategy for the distribution's shape. This performance
521 was further verified in Figure 5, which depicted the match relationships between qualities in
522 both identifications and validations (overall RMSE) and model's degrees of freedom (D_f). As
523 noticed, even though four- and five-Gaussian had lower RMSE values during model
524 identifications, their prediction abilities were inferior to two Gaussian+ one exponential
525 DAEM. On the other hand, three-Gaussian and three-logistic DAEM had identically small D_f
526 as two Gaussian + one exponential DAEM, yet they both demonstrated worse prediction

527 potentials. Two Gaussian and one exponential successfully located both its RMSE and D_f in
 528 the low ‘optimal zone’ (highlighted with the red circle), which ensured accurate prediction
 529 ability while avoiding excessive numerical complexity. In this sense, two-Gaussian and one
 530 exponential provided the best trade-off between prediction ability and degrees of freedom.



531 Figure 5. Degrees of freedom and overall RMSE in both identification and validation of five
 532 types of DAEM

533
 534 Independent and global first-order reaction mechanism was additionally considered
 535 herein for comparison purpose. This kinetic method often worked for simple approximation
 536 that treated biomass as single or multiple pseudo-components [55, 56], in which each set of
 537 kinetic equation (Arrhenius equation) required at least two independent parameters, i.e. pre-
 538 exponential factor and global activation energy. Becidan [57] claimed 7 to 8 partial reactions
 539 were required for acceptable fit, in other words, it needed 8 to 9 independent parameters with
 540 assumption that they shared same pre-exponential factor, which was still too complicated. Its
 541 limited reaction types were unlikely appropriate descriptions of the infinite number in real
 542 pyrolysis. Worse still, the mechanism faced poor applicability in fitting multiple temperature

543 profiles [40, 57]. Yet in two-Gaussian + one exponential DAEM, 10 parameters were
 544 sufficient to capture essences of massive reactions, being adequately concise and meantime
 545 powerful. From this perspective, the proposed two-Gaussian + one exponential again
 546 presented as excellent model choice for kinetic determinations.

547 To further confirm the superiority of two-Gaussian + one exponential DAEM, three-*nth*-
 548 order mechanism was also applied for comparison [58]. Herein, pre-exponential factor (A)
 549 was assumed identical in three reactions, and each scheme had its specific activation energy
 550 (E) and reaction order (n). The superposition of three *nth*-order reaction schemes was
 551 subsequently fitted in both dynamic and static tests for parameter identification and
 552 verification (table 8). Regarding the overall RMSE in identification, three-*nth*-order model
 553 had much larger deviation than in two-Gaussian + one exponential DAEM (RMSE= $7.6 \times$
 554 10^{-5}), revealing worse fitting quality. More importantly, this model had worse prediction
 555 capacity compared to two-Gaussian + one exponential DAEM (RMSE= 2.0×10^{-4} in
 556 validation), yet its numerical complexity was hardly simplified ($D_f = 10$), which again
 557 supported the better performances of proposed DAEM.

558 Table 8. Identified parameters of three-*nth*-order model and overall RMSE in
 559 identification and validation stages

Pseudo-component	V_{max}	A (s^{-1})	E (kJ/mol)	n	Overall RMSE in identification	Overall RMSE in validation
First	0.3234		152.88	0.83		
Second	0.4728	2.98×10^{11}	165.53	1.10	1.9×10^{-4}	4.5×10^{-4}
Third	0.2931		227.95	0.69		

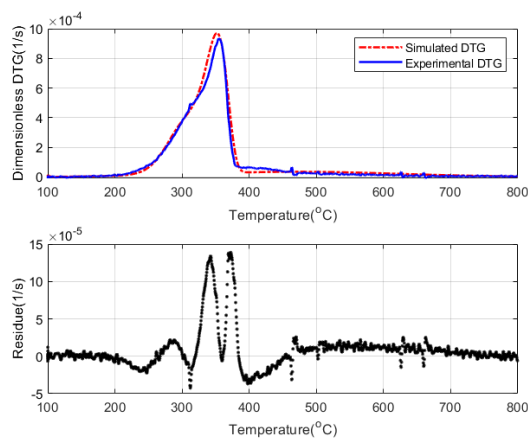
560

561 4.3 DTG simulation

562 DTG simulations were conducted to assess the performance of different distributions in
 563 the five comparable DAEMs. Figure 6 illustrated DTG simulations by the overall model and
 564 individual distributions at 5 °C/min. The heating rate was chosen due to its moderate baseline
 565 fluctuations; DTG simulations at other heating rates are within the supplementary material. It

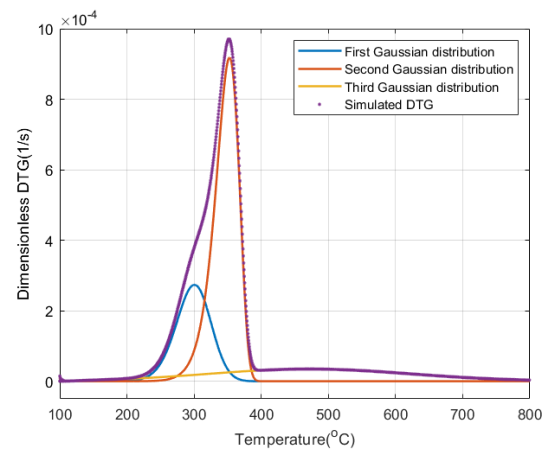
566 was obvious that the overall DTG simulations of five models overlapped substantially with
567 experimental data, and the only visible deviations occurred near the DTG peak. For analysis,
568 the main variations of local residue ($R_L(t)$) were manually divided into three noticeable
569 sections here, ranging between 100–300, 300–400 and 400–800 °C, respectively. The first and
570 third sections moderately fluctuated, and hemicellulose decomposition was mainly attributed
571 to the first. Meanwhile, lignin decomposition and secondary reactions were responsible for
572 the third section [59]. The second section showed the most severe fluctuations with two
573 obvious peaks; they were believed to originate from the mixed pyrolysis of hemicellulose and
574 cellulose [60]. Cellulose decomposed rapidly within a very narrow temperature range after its
575 crystallites melted [61] and it partially merged with hemicellulose. Inevitably more detectable
576 errors emerged in this section during simulations.

Overall DTG with local residues

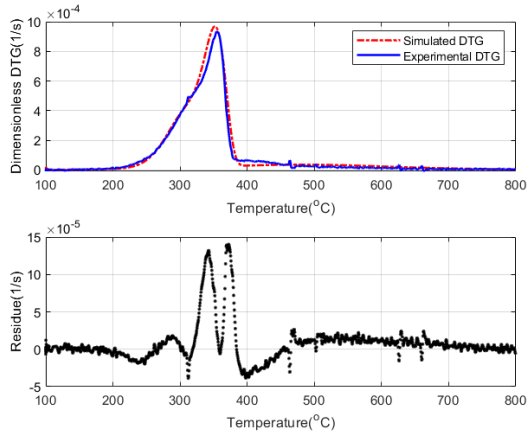


Three-Gaussian
DAEM

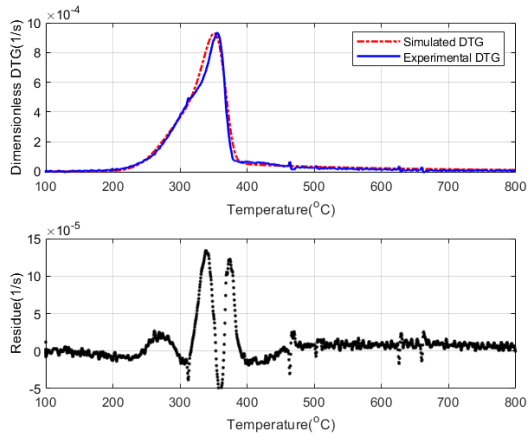
Separate and overall DTG



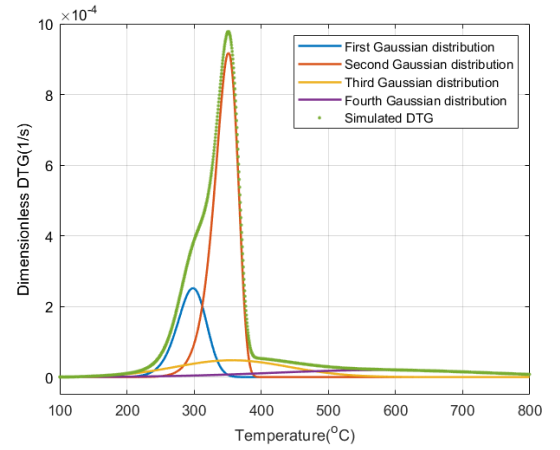
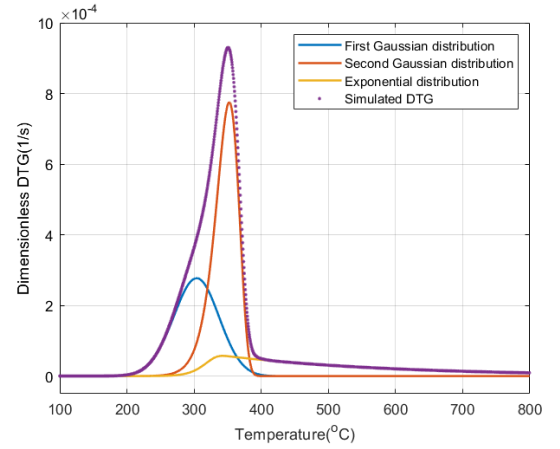
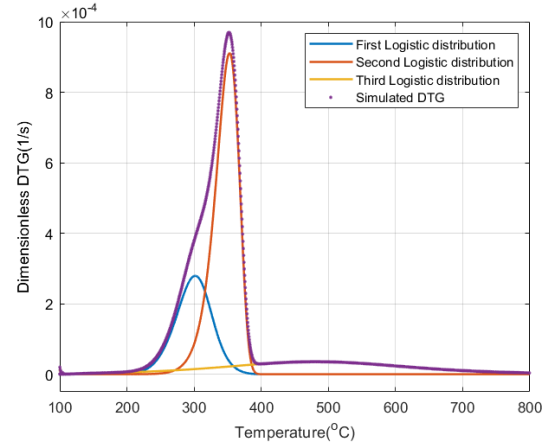
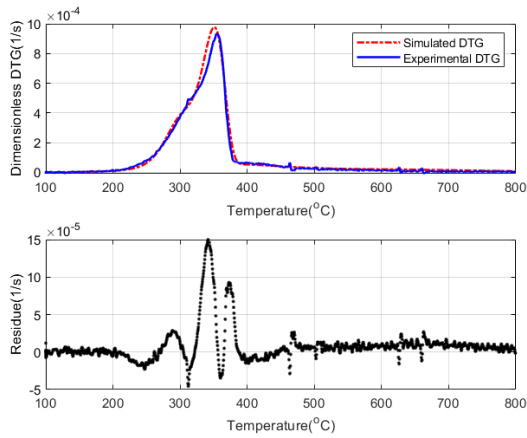
**Three-Logistic
DAEM**



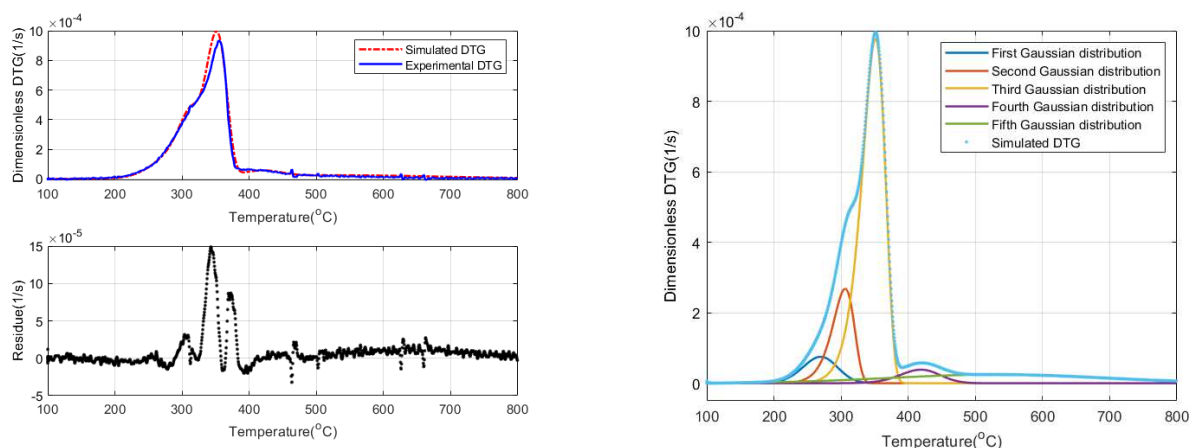
**Two Gaussian
+one exponential
DAEM**



**Four-Gaussian
DAEM**



Five-Gaussian
DAEM



577 Figure 6. Experimental, simulated DTG curves and corresponding local residues (left),
578 separate and overall DTG simulations (right) of five DAEM at the heating rate of 5 °C/min

579

580 Standard deviations (σ_R) of sectional simulations were compared in Table 9. Among the

581 DAEMs with three distributions, two Gaussian + one exponential DAEM exhibited the best

582 simulation improvements, especially in the third section wherein the asymmetric exponential

583 uniquely functioned. Further compared to two Gaussian + one exponential DAEM, four-

584 Gaussian DAEM showed only slight improvements in first and second sections, and five-

585 Gaussian DAEM improved in all three sections. However, as previously emphasized, it was

586 not practical nor feasible to increase numerical complexity for limited error improvement.

587 Using the two Gaussian + one exponential DAEM as a reference, the error reduction ratios in

588 three sections realized by four-Gaussian DAEM were 4.34 %, 1.60 %, 0 %, respectively, and

589 42.03 %, 10.49 %, 8.33 %, respectively, by five-Gaussian DAEM. The five-Gaussian DAEM

590 provided the only notable improvement in the first section, which represented a very small

591 part of pyrolysis kinetics. So, here the asymmetric exponential distribution again presented a

592 good trade-off strategy to improve accuracy and maintain numerical concision.

593

594 Table 9. The sectional standard deviation of DTG residue at the heating rate of 5°C/min
 595 of five models

Temperature section (°C)	$\sigma_R (\times 10^{-6})$				
	Three-Gaussian	Three-Logistic	Two Gaussian+one exponential	Four-Gaussian	Five-Gaussian
100–300	7.2	7.4	6.9	6.3	4.0
300–400	57.3	57.3	56.2	55.3	49.5
400–800	11.9	12.2	7.2	7.2	6.6

596
 597 Separate DTG simulation further depicted each pseudo component's contribution to the
 598 overall decomposition rate (right row of Figure 6). The three-Gaussian and three-logistic
 599 DAEMs had same decomposition ranges of three pseudo-components: 200–375 °C (first
 600 pseudo-component), 250–400 °C (second pseudo-component) and 100–800 °C (third pseudo-
 601 component). Compared to these two models, two Gaussian + one exponential DAEM altered
 602 the decomposition range of first pseudo-component (200–400 °C), induced no change for
 603 second pseudo-component (250–400 °C), and increased initial decomposition temperature of
 604 the third pseudo-component (270–800 °C). For the four-Gaussian DAEM, four pseudo-
 605 components decomposed in the temperature ranges as 220–360, 250–400, 160–550 and 100–
 606 800 °C respectively. Finally, the decomposition temperature ranges of five-Gaussian DAEM's
 607 pseudo-components were: 165–375, 200–350, 240–400, 280–520 and 100–800 °C,
 608 respectively.

609 It was always worthwhile to identify pseudo-components as the signatures of major
 610 chemical components. The totality of specific species could be described by one unique
 611 distribution, and further assist in understanding the multi-component mechanism of biomass
 612 pyrolysis. In this vein, Table 10 shows relevant thermogravimetric decomposition
 613 temperatures of the three main constituents in biomass. Generally, hemicellulose consists of
 614 polysaccharides that are heterogeneously branched and are non-covalently bonded to the

615 surface of cellulose microfibril [62]. The less stable chemical structures make hemicellulose
616 more reactive with lower temperature ranges of decomposition. Cellulose is a saturated linear
617 polysaccharide with high polymerization and degree of crystallinity and decomposes in very
618 narrow temperature ranges [63]. Lignin is a set of irregular phenolic polymers consisting of
619 more than four substituted phenyl propane, which endow lignin with large decomposition
620 ranges during the entire pyrolysis process [64]. Many published values provided reliable
621 references for featuring pseudo-components. By comparing chemical constituents'
622 decomposition temperatures with model calculations, it was, therefore, feasible to correspond
623 the three pseudo-components to hemicellulose, cellulose and lignin respectively in the three-
624 Gaussian, three-logistic and two Gaussian + one exponential DAEM, which were well-
625 accepted strategies [6, 34, 65]. For the four-Gaussian DAEM, first and second pseudo-
626 components were linked with hemicellulose and cellulose, while the third and fourth pseudo-
627 components possibly presented the two-stage decomposition scheme of lignin [66]. In the five
628 -Gaussian DAEM, the first and second pseudo-components together represent hemicellulose,
629 then the third pseudo-component was assigned to cellulose. The fourth and fifth components
630 were attributed to two overlapped partial reactions, the scission of oxygen functional groups
631 and rearrangement of the carbon skeleton were believed responsible for these two
632 distributions, respectively [48].

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639 Table 10. Summary of individual biomass component's decomposition temperature range

Heating rate (°C/min)	Decomposition temperature range (°C)			Reference
	Hemicellulose	Cellulose	lignin	
10	220–315	315–400	>400	[67]
10	200–320	280–360	140–600	[68]
20	200–350	260–430	200–500	[69]
20	253–308	319–368	259–482	[70]
20	244–324	294–371	197–653	[71]
50	250–350	350–500	>500	[72]
60	200–327	327–450	200–550	[2]
<5	225–325	324–375	250–500	[73]

640

641 Peak temperatures observed in both experimental and simulated DTG at different heating
642 rates are listed in Table 11. The peak temperatures corresponded to the extreme reaction stage
643 of cellulose decomposition, and they followed a decreasing trend with an increase of heating
644 rate, which was caused by the altered pyrolysis kinetics relating to inter-particle heat transfer
645 [74]. In general, five models reproduced the peak temperatures accordingly at four heating
646 rate conditions, with considerably small errors less than 5 °C. It was clear that multiple-
647 distribution DAEMs were capable of distinguishing the effects of heating rates, which has
648 rarely been observed in relevant researches. Peak values were usually applied in Kissinger
649 procedure for determining activation energy [75], as a direct and easy method. However, its
650 limitations arose in merely staying at observation stage based on existing experimental data.
651 By comparison, multiple-distribution DAEMs herein presented a precise description of peak
652 temperatures and confirmed the prediction abilities already proved on mass loss. Therefore, it
653 would be safe to conclude that the proposed models could advance one step further as
654 prediction tools in isoconversional kinetics. DAEM may be applied for the accurate
655 description of global pyrolysis kinetics under different reaction conditions.

656

657 Table 11. Peak decomposition temperature from experiments and model simulations

Heating rate (°C/min)	Experimental	Three-Gaussian	Three-Logistic	Two Gaussian+ one exponential	Four-Gaussian	Five-Gaussian
1	366.58	363.58	363.58	362.59	362.59	362.59
2	354.73	351.73	352.23	350.73	350.73	351.23
5	339.06	337.08	337.08	335.88	336.08	336.48
10	329.44	326.64	326.64	325.13	325.43	325.83

658

659 **Conclusion**

660 A rigorous strategy of both identification and validation was applied in the DAEM for
661 analysing the effects of distribution number and shape. First, in a series of Gaussian-DAEMs
662 with distribution number ranging from one to five, three-distribution was determined as the
663 best trade-off between prediction ability and degrees of freedom. Logistic and exponential
664 distributions were proposed to account for distribution shapes. Exponential distribution
665 allowed good simulations for high-temperature reactions, and together with two Gaussian
666 distribution, they exhibited as the best strategy in terms of both prediction capacity and
667 numerical concision. The overall DTG simulation at 5 °C/min was analysed within three
668 major variation sections, where two-Gaussian + one exponential DAEM achieved obvious
669 error reduction with plausible numerical concision. Degradation temperature ranges by
670 separate DTG simulations evidenced the correspondences between pseudo-components and
671 chemical components, and DAEM's was able to distinguish the effect of heating rate on the
672 peak decomposition temperature.

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677

678 **Reference**

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